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An Analysis of Transcrystallinity in Polymers

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Abstract. Polymer crystallization often occurs in the presence of foreign bodies, such as walls of processing tools. In such cases, there is a competition between nucleation in the bulk polymer and nucleation on well-identified surfaces. If many nuclei are activated at the surfaces, their proximity imposes that entities emanating from these nuclei grow preferentially normal to the surfaces, leading to transcrystalline zones. The competition between surface and bulk nucleation can be studied through crystallizations of thin polymer films in contact with pan surfaces in a DSC apparatus. These experiments show that in thin samples transcrystallinity is limited by sample thickness. When thickness increases, the transcrystalline zones can grow, but up to a limiting value, because at a certain stage their development is stopped by the growth of bulk spherulites. A specific analysis of these DSC experiments gives access to crystallization parameters such as the number of nuclei per unit surface or the growth rate, and makes it possible to determine the crystallization kinetics of the polymer not disturbed by transcrystallinity.

THE CONCEPT OF TRANSCRYSTALLINITY

In many cases, polymer crystallization occurs in the presence of well-identified foreign bodies, such as processing tools (molds, calibrators, chill-rolls), laboratory equipment (glass slides, calorimetry pans), fillers (e.g., CaCO₃), reinforcing materials (e.g., natural or synthetic fibers), pigments, nodules in blends, or nucleating agents, i.e., substances added on purpose to promote intense heterogeneous nucleation. In such cases, there is a competition between nucleation in the bulk polymer (volume nucleation) and heterogeneous nucleation on the well-identified surfaces (surface nucleation). Three types of behavior can be distinguished: (i) inactivity of surfaces: spherulites appear only in the polymer volume; (ii) medium activity of the surfaces: a few half-spherulites are created from surface nuclei; (iii) high activity of the surfaces: if many heterogeneous nuclei are activated at the surfaces, their proximity imposes that entities emanating from these nuclei grow preferentially normal to the surface, leading to what is usually called transcrystalline zones (Fig. 1a).

This interpretation of transcrystallinity, due to Fitchmun and Newman [1], is based only on geometrical considerations, and does not require the occurrence of flow or temperature gradients. It is confirmed by numerical simulations in which a sufficiently high number of nuclei are added on the surfaces [2]. The program calculates the boundaries between semi-crystalline morphologies, which makes it possible to reproduce the transcrystalline regions as well as their intersections with isolated bulk spherulites (Fig. 1b).

The competition between surface and bulk nucleation can be appropriately studied through crystallizations of thin polymer films in contact with aluminium pans surfaces in a DSC (Differential Scanning Calorimetry) apparatus. From a careful analysis of the experimental data, it is possible to derive original methods, which give access to crystallization parameters (number of nuclei per unit surface, growth rate), and allow us to determine the crystallisation kinetics of the polymer itself, that is, not disturbed by transcrystallinity. This analysis of transcrystallinity has been applied to different polymers: polyamide 6-6 (PA66) and high density polyethylene (HDPE).

This paper is both a review of previous work in our laboratory and a presentation of some results obtained recently.

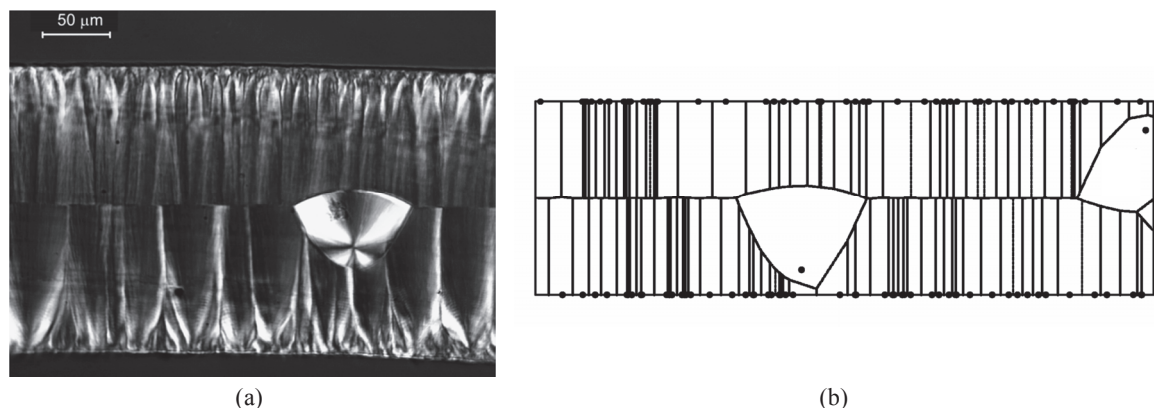


FIGURE 1. (a) Transcrystalline regions in a PA66 film. Only one bulk spherulite is visible; (b) Reproduction of transcrystalline regions by computer simulation. From [2]

STUDY OF TRANSCRYSTALLINITY IN DSC EXPERIMENTS

Experimental Results

A first series of experiments conducted with PA66 [3] showed that important transcrystalline regions corresponded to coarse spherulites at the specimen core. Conversely, thin transcrystalline regions were associated to large number of small spherulites at the core. A second series of experiments was then performed with HDPE films of different thicknesses ranging from 192 to 865 μm [4]. All the samples had important transcrystalline zones at their surfaces. Thin samples were almost completely overlapped by transcrystalline regions. Medium-thickness samples contained more volume spherulites, but one row of spherulites to the maximum appeared in their mid-plane. Thick samples, for their part, contained two larger spherulites in the part of the thickness which was not overlapped by transcrystalline zones. The total thickness of the transcrystalline zones and the maximum diameter of the bulk spherulites both increased up to a maximum value of about 350 μm, which was reached for the same sample thickness [4,5]. These results show that in thin samples the transcrystalline thickness is mainly limited by the sample thickness. The higher the thickness, the more important the transcrystalline zones up to a certain value, because in thick samples volume spherulites are more numerous and stop the development of transcrystallinity.

The two types of morphologies observed in the first series of experiments with PA66 corresponded to two different shapes of the crystallization traces recorded by DSC [3]: curves exhibiting a more or less pronounced shoulder and curves showing a single crystallization peak. The thermograms with a shoulder corresponded to important transcrystalline regions and coarse spherulites at the specimen core. Conversely, the thermograms which exhibit a single peak were associated with thin transcrystalline regions and a large number of small spherulites at the core. Consequently, the shoulder was correlated to transcrystallinity and to the competition between surface and volume nucleation. This assumption was checked by experiments on nucleated PA66: when a nucleating agent nucleation, promoting volume nucleation, is added to the polymer, the shoulder-shaped peak becomes a single one, and its maximum is shifted towards higher temperature [6].

Numerical Simulation

Numerical simulation allows us to reproduce both the microtomed sections and the DSC peaks [6]. Three cases have been considered: (1) no volume nuclei; (2) a few volume nuclei; (3) many volume nuclei. In the second case, the main peak is preceded by a shoulder which disappears in the third one. This is in agreement with the effects of a nucleating agent: increasing the number of core spherulites displaces the main peak towards higher temperatures and makes the shoulder disappear.

In the first case (no volume nucleation), the shoulder remains present. The different steps of the development of transcrystallinity were followed through the calculation of planar sections parallel or perpendicular to the sample surfaces. At the very first steps of the transformation, the transformed volume consists of distinct semi-spherical spherulites. As the spherulites grow, their growth is progressively limited to directions more or less perpendicular to the surfaces. Step by step, the transformed volume becomes more “compact” and finally, the transformation is achieved by the propagation of two continuous fronts. This change from half-spheres to continuous fronts is responsible for the shoulder observed in the DSC traces. This analysis confirms that the shoulder at the beginning of the DSC peaks can be unambiguously related to the transcrystalline zones.

ORIGINAL METHODS FOR THE DETERMINATION OF CRYSTALLIZATION PARAMETERS

The analysis of the crystallization peaks developed in the previous section makes it possible to propose original methods for the determination of some crystallization parameters [7].

At sufficiently high transformed volume fraction α , there are two continuous fronts and α is given by:

$$\alpha(t) = \frac{2}{e} \int_0^t G(u) du \quad (1)$$

hence:

$$T_p e \frac{d\alpha}{dT} = 2G(T) \quad (2)$$

where T is the temperature, T_p the cooling rate and e the sample thickness. As a consequence, experimental values of $0.5 T_p e d\alpha/dT$ give access to the growth rate $G(T)$.

Coming back to low transformed volume fractions and assuming an instantaneous surface nucleation, the very first steps of the transformation (semi-spherical spherulites) can be described by:

$$\alpha(t) = \frac{4\pi}{3} \frac{N_s}{e} \left[\int_0^t G(u) du \right]^3 \quad (3)$$

which makes it possible to determine the number of nuclei per unit surface N_s , if the growth rate is known.

In order to characterize bulk crystallization, the transformed volume V_{tran} is decomposed into the volume V_{sur} overlapped by transcrystallinity and the volume V_{vol} occupied by bulk spherulites:

$$V_{tran} = V_{sur} + V_{vol} = \alpha V_{tot} \quad (4)$$

where V_{tot} is the total volume of the sample. The bulk crystallization can be characterized by α_v , fraction of the volume which would be transformed if there were no transcrystallinity:

$$\alpha_v = \frac{V_{vol}}{V_{tot} - V_{sur}} \quad (5)$$

which leads to:

$$\alpha = \alpha_v + (1 - \alpha_v) \frac{d}{e} \quad (6)$$

where d is the total thickness of the transcrystalline zones. So, when αe is plotted versus sample thickness at given temperature and cooling rate, it should obey a linear variation, with a slope α_v .

In conclusion, it is possible to treat DSC experiments when important transcrystalline zones exist. New methods are now available, which give access to crystallization parameters such as the number of nuclei per unit surface or the growth rate, and make it possible to determine the crystallization kinetics of the polymer not disturbed by transcrystallinity. These methods have been applied to HDPE [7] and PA66 [8].

APPLICATIONS

HDPE [7]

Experiments were conducted with a HDPE ($M_w = 39,000$ g/mol, $M_n = 10,800$ g/mol, density = 0.9574 g/cm³). Experimental values for the parameter $0.5 T_p e d\alpha/dT$ are plotted versus temperature using 18 different cooling rates in Fig. 2a. Despite a certain scatter the values are roughly organized in a master curve, which should represent the growth rate of spherulites, according to Eq. 2. It is possible to fit these data using the following expression:

$$G(T) = G_0 \exp\left(-\frac{A}{T(T_{m0} - T)}\right) \quad (7)$$

where G_0 , A and T_{m0} are constants, T_{m0} being the equilibrium melting temperature. Four different fits are shown in Fig. 2a, corresponding to four sets of parameters:

set 1: $G_0 = 25,000$ $\mu\text{m/s}$, $A = 112,000$ K², $T_{m0} = 418$ K;

set 2: $G_0 = 288.1$ $\mu\text{m/s}$, $A = 28,202$ K², $T_{m0} = 404$ K;

set 3: $G_0 = 25,000$ $\mu\text{m/s}$, $A = 106,000$ K², $T_{m0} = 418$ K;

set 4: $G_0 = 25,000$ $\mu\text{m/s}$, $A = 103,000$ K², $T_{m0} = 418$ K.

The best mathematical agreement is obtained for set 2. Unfortunately, this leads to a too low equilibrium melting temperature. Therefore, a more realistic value of T_{m0} (418 K) was imposed, and new values of G_0 and A were calculated. Sets 1 and 4 correspond to the bounds of the experimental values of G , whereas set 3 leads to an agreement equivalent to that obtained with set 2.

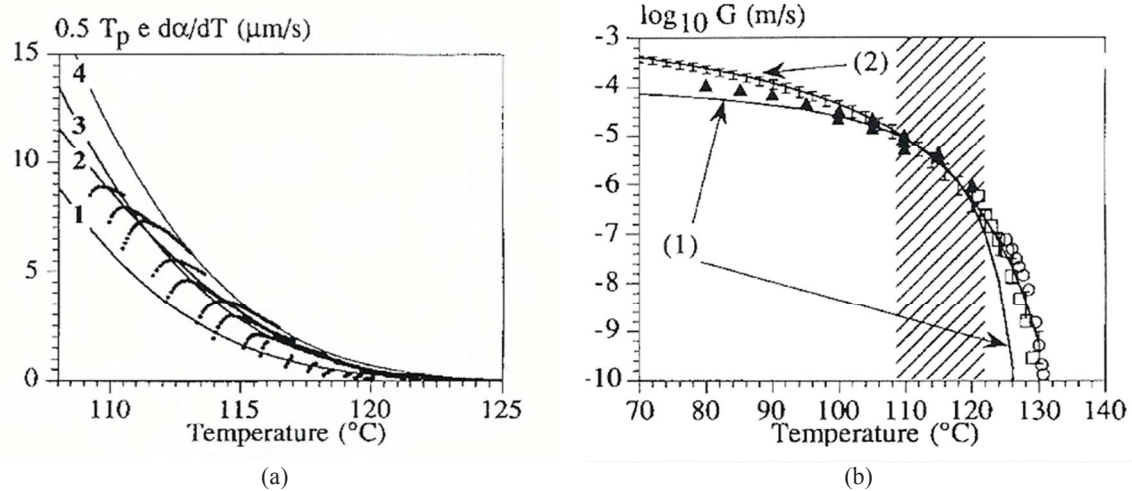


FIGURE 2. Determination of growth rate: (a) Experimental values for $0.5 T_p e d\alpha/dT$ vs. temperature (symbols) and four different mathematical fits; (b) Evolution of $\log G$ vs. temperature. Comparison of experimental data from the literature (symbols) and our estimates (curves 1 and 2, corresponding to sets 2 and 3, respectively) [7]

Equation 7 used with the two best sets of parameters determined above (sets 2 and 3) has been compared to some experimental data reported in the literature (Fig. 2b). The hatched region represents the range of temperature in which G has been estimated. It can be concluded that the two sets lead to a good agreement with literature in that range. Moreover, extrapolations towards either higher or lower temperature are also in pretty good agreement with reported experimental data, especially when set 3 is used (curve 2). Errors bars in Fig. 2b correspond to sets 1 and 4.

PA66 [8]

More recently, the same experiments were performed with a PA66 ($M_n = 38,690$ g/mol), with the same procedures of interpretation. Figure 8 shows the crystallization curves obtained for three sample thicknesses: (1) 162 μm , (2) 346 μm and (3) 610 μm . The thinnest sample is completely overlapped by transcrystallinity. The second sample contains one row of spherulites at the core, whereas more numerous bulk spherulites are observed in the third one. The three DSC curves exhibit the shoulder-shaped character associated with transcrystallinity (Fig. 3) and it is possible to superpose their high-temperature parts.

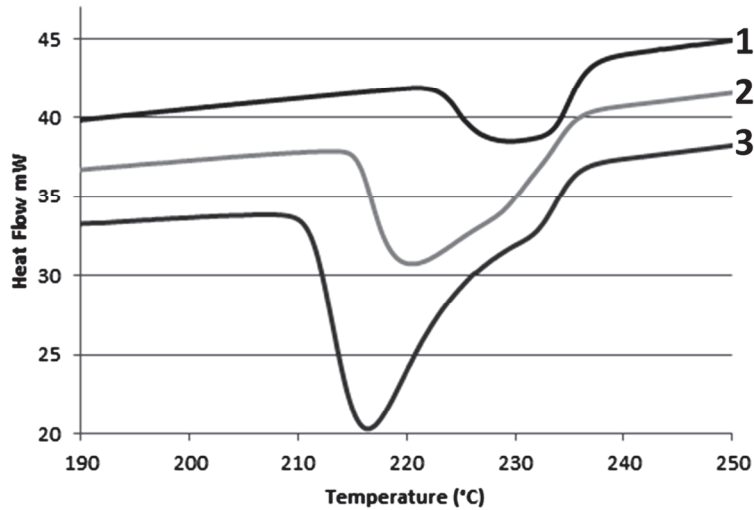


FIGURE 3. DSC crystallization curves of PA66 at a cooling rate of 10 K/min for different sample thicknesses: (1) 162 μm , (2) 346 μm and (3) 610 μm

Growth rate has been determined as indicated above for cooling rates ranging from 1 to 700 K/min, and a figure analogous to Fig. 2b for HDPE has been obtained. Once more, there is a correct agreement between our data and literature [9]. According to Eq. 6, α_e is plotted versus sample thickness in Fig. 4a, at a cooling rate of 10 K/min and for different temperatures. At any temperature, a straight line is obtained, whose slope α_v increases from 0 to a maximum of 1 when the temperature decreases. Using this procedure, it is possible to determine α_v as a function of temperature. This estimate seems to be qualitatively correct since the general form of the transformation curves is reproduced. Figure 4b makes it possible to appreciate the difference between the “true” overall kinetics α_v and the kinetics perturbed by more or less important transcrystallinity.

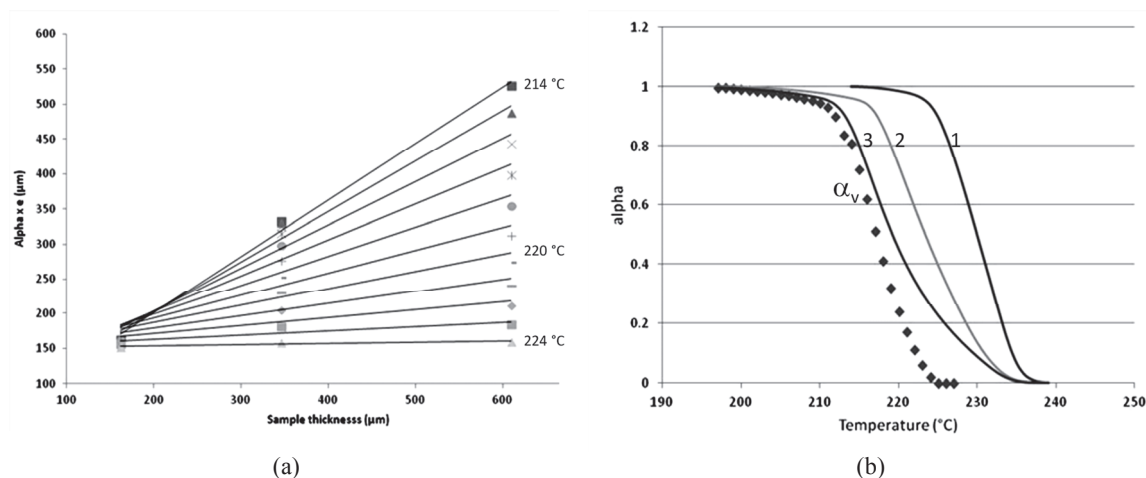


FIGURE 4. Determination of bulk crystallization at a cooling rate of 10 K/min: (a) α_e vs. sample thickness for different temperatures ranging from 214 to 224 °C; (b) Evolution of bulk transformed volume fraction α_v vs. temperature (squares), and comparison with the kinetics for the three specimens exhibiting transcrystallinity: (1) thickness 162 μm , (2) thickness 346 μm and (3) thickness 610 μm

CONCLUSIONS

DSC experiments can be used as model experiments to study transcrystallinity in thin polymer films. Varying the specimen thickness enables us to analyze the competition between surface nucleation and volume. Thus, in thin samples transcrystallinity is limited by the sample thickness. When thickness increases, the transcrystalline zones can grow, but up to a limiting value, because at a certain stage their development is stopped by the growth of bulk spherulites. The occurrence of transcrystallinity modifies the shape of crystallization curves, which exhibit a more or less pronounced shoulder. A change in the type of growth, from half-spheres to continuous fronts, is responsible for this shoulder observed in the DSC traces

A specific analysis of these DSC experiments gives access to crystallization parameters such as the growth rate of semi-crystalline entities. In spite of a certain degree of uncertainty, the results obtained by this new method compare well with already published data. This method is particularly of interest when direct observation of spherulites is impossible.

It is also possible to determine the “intrinsic” crystallization kinetics of the polymer, i.e., not disturbed by transcrystallinity. This method has been applied to HDPE and to PA66. The kinetics obtained could be influenced by volume limitation, due to the small thickness of the specimens. This effect should not be too important here, since our experimental plots are in correct agreement with the corresponding theoretical expressions (linear plots). Nevertheless, theoretical developments should be necessary to appreciate the exact effect of confinement.

Indeed, another route to study both confinement and transcrystallinity effects is to model the overall kinetics in a thin film with and without transcrystallinity. Different models have been established in our laboratory [3,10-13] and could be used for that purpose.

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